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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Production of Titanium Dioxide

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A PROCESS FOR THE PRODUCTION OF TITANIUM DIOXIDE

Abstract of the Disclosure

A process for the production of titanium dioxide by the sulfate process in which the liquid accumulating during washing of the titanyl sulfate hydrolysis hydrolyzate is fractionated and the dilute fractions are returned to the process while the relatively concentrated thin acid is fed to a waste disposal.

A PROCESS FOR THE PRODUCTION OF TITANIUM DIOXIDE

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This invention relates to a process for the production of titanium dioxide by the sulfate process, in which the liquid accumulating during washing of the hydrolyzate is fractionated and the dilute fractions are returned to the process while the relatively concentrated waste acid is fed to a recycling process.

It is known that, apart from raw material and process costs, the economy of titanium dioxide production is being increasingly influenced by the costs involved in treatment of the waste acid and by government-imposed wastewater levies. Accordingly, various processes have already been proposed with a view to reducing treatment costs by increasing the concentration of the waste acid or by directly recycling waste acid to the process. According to US 4,502,976, a waste acid of high concentration is separated from dilute washing acid through careful monitoring of the sulfuric acid concentration in the liquid accumulating during washing of the hydrolyzate. This dilute washing acid may advantageously be concentrated, optionally in part, by waste heat in a first evaporation stage.

According to DE-C 2,729,755, ilmenite is digested with a mixture of 62 to 75% sulfuric acid, recovered by concentration of waste acid by evaporation and separation of the metal sulfates, and at least 95% pure sulfuric acid and the digestion cake is dissolved with water and part of the waste acid formed during the

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5 hydrolysis of titanyl sulfate. However, this process is specially designed for the use of ilmenite as raw material, in addition to which narrow limits are imposed by the metal sulfates, particularly chromium sulfate, recycled with the waste acid.

10 Another major disadvantage of this process is that the TiO_2 production process is seriously impaired by the very high proportion of waste acid (20 to 30%) used to dissolve the digestion cake. If the quantity of sulfuric acid used to digest the raw material is correspondingly reduced, a lower yield of TiOSO_4 is obtained when the
15 autothermal discontinuous digestion reaction is carried out on an industrial scale. If, on the other hand, the $\text{H}_2\text{SO}_4:\text{TiO}_2$ ratio is kept constant during the digestion reaction, such a high $\text{H}_2\text{SO}_4:\text{TiO}_2$ ratio is obtained in
20 the titanyl sulfate solution through the waste acid used to dissolve the digestion cake that the hydrolysis yield and the TiO_2 pigment properties are adversely affected.

Accordingly, the problem addressed by the present invention was to provide a process by which it would be possible, both with ilmenite and with titanium slag as
25 raw material, to obtain a maximal proportion of the sulfuric acid used to digest the titanium raw material as highly concentrated waste acid from the process, thereby minimizing both treatment costs and wastewater pollution, without adversely affecting the process as
30 a whole or the quality of the titanium dioxide pigment.

The present invention relates to a process for the production of titanium dioxide by digestion of titanium raw materials with sulfuric acid, dissolution of the

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5 digested material to form a titanyl sulfate solution,
hydrolysis of the titanyl sulfate, separation of the
hydrolyzate from the metal-sulfate-containing sulfuric
acid, the so-called waste acid, washing of the hydroly-
zate and calcination to the TiO_2 pigment, the solution
10 accumulating during separation of the solids from the
suspension formed during hydrolysis of the titanyl sul-
fate being fed entirely as waste acid to a treatment or
recycling process and the liquid accumulating during
washing of the hydrolyzate being divided into three or
15 four fractions of decreasing sulfuric acid concentra-
tion, the first fraction A accumulating being combined
with the waste acid and fed to the treatment or re-
cycling process, the second fraction B accumulating
thereafter being used instead of water in the hydrolysis
of the titanyl sulfate, the third fraction C being used
20 to dissolve the digested material formed during di-
gestion of the titanium raw material and, optionally,
a fourth fraction D being used instead of water to wash
the hydrolyzate or being removed as wastewater.

25 In a particularly preferred embodiment of the pro-
cess, the waste acid fed to the treatment or recycling
process has a concentration of at least 23% by weight
 H_2SO_4 and preferably of at least 24% by weight H_2SO_4

The fraction B returned to hydrolysis of the titanyl
sulfate from washing of the hydrolyzate preferably contains
30 7 to 23% by weight H_2SO_4 and the fraction C used to dissolve
the digested material 0.2 to 7% by weight H_2SO_4 .

In one preferred embodiment of the process, hydrolysis
of the titanyl sulfate is carried out using separately

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5 produced hydrolysis nuclei and fraction B is only added
after at least 50% of the total duration of the hydrolysis
process has elapsed.

Accordingly, the liquid accumulating during washing of
the hydrolyzate is divided up into three or, optionally,
10 four fractions according to the sulfuric acid concentra-
tion. These fractions are then specifically returned to
the process or are removed.

More particularly, the process comprises the following
steps:

15 Titanium raw materials, particularly ilmenite or
titanium slag, are digested in known manner with 80 to 95%
sulfuric acid. The sulfuric acid used is preferably a
mixture of at least 95% sulfuric acid or oleum and at least
60% sulfuric acid recovered by concentration of waste
20 acid from the sulfate process by evaporation and sepa-
ration of the metal sulfates from the sulfuric acid.
Alternatively, sulfuric acid recovered from waste acid
by other recycling processes may also be used.

According to the invention, the preferably solid
digested material which accumulates during digestion of the
25 raw material is dissolved with the third fraction C of the
solution accumulating during washing of the hydrolyzate.
The fraction in question has an H_2SO_4 content of 0.2 to 7%
by weight. Water or other solutions containing sulfuric
acid may be used together with fraction C.

30 The low concentration of fraction C rules out any
adverse effect on the subsequent hydrolysis process or on
the pigment quality.

Solids and, optionally, iron sulfate heptahydrate are
separated off in known manner from the titanyl sulfate
35 solution obtained.

5 Subsequent hydrolysis of the titanyl sulfate is
carried out, for example, using separately produced
hydrolysis nuclei, fraction B accumulating during
washing of the hydrolyzate being added to the solution.
Fraction B is preferably added after at least 50% of the
total duration of the hydrolysis process has elapsed.
10 The quantity of fraction B is gauged in such a way that
the suspension contains 160 to 200 g (TiO₂/l at the end
of the hydrolysis process. The addition of fraction B
containing 7 to 23% by weight H₂SO₄ in accordance with
the invention does not adversely affect pigment quality.
15 However, the concentration of the waste acid is
distinctly increased in relation to the concentration
obtained where water is added in accordance with the
prior art.

20 The hydrolyzate is separated, optionally by filtra-
tion, from the mother liquor, the waste acid containing
H₂SO₄ and metal sulfates, and subsequently washed with
water. The concentration of H₂SO₄ and metal sulfates of
the solution, which accumulates during this washing of
the hydrolyzate, changes characteristically during the
25 washing process. Initially, waste acid is displaced from
the hydrolyzate by the washing water. The sulfuric acid
concentration then falls slowly from the range of 24-27%
by weight to values of 18 to 23% by weight. According
to the invention, this concentrated solution is fed as
30 the first fraction A to the waste acid until the H₂SO₄
concentration of the solution flowing off has fallen to
a value in the range of 24-15% by weight. The waste acid
thus obtained contains 85 to 97% of the sulfate ions

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5 contained in the titanyl sulfate solution after separation of iron sulfate heptahydrate, corresponding to 80-93% of the sulfuric acid present in the suspension after hydrolysis of the titanyl sulfate. A fraction B is then separated off while the H_2SO_4 concentration falls rapidly from 25-15 to 12-3% by weight. According to the
10 invention, this fraction B with an average H_2SO_4 content of 10-23% by weight contains 4-12% of the sulfuric acid present after hydrolysis and, as described above, is added during hydrolysis of the titanyl sulfate. The relatively highly dilute solution accumulating after the
15 steep fall in concentration to less than 12% by weight H_2SO_4 is separated as the third fraction C. According to the invention, this fraction C with, on average, 0.2-7% by weight H_2SO_4 contains 1 to 5% of the sulfuric acid present after hydrolysis and is used to dissolve the
20 digested material. A highly dilute fourth fraction D is optionally used instead of water to wash the hydrolyzate or is removed as wastewater. According to the invention, it contains less than 5% and preferably less than 1% of the sulfuric acid present after hydrolysis.

25 Whereas, according to DE-C-2 729 755, it is only possible to obtain a waste acid concentration of 21-23% by weight H_2SO_4 and problems can be expected from the metal ions relevant to color of the pigment, particularly Cr or V ions, present in the recycled solutions, it
30 has surprisingly been found that neither the titanium dioxide production process itself nor the quality of the pigment obtained is adversely affected by application of the process according to the invention. A major

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5 advantage of the invention is that it gives a waste acid
of high concentration both where ilmenite and where
titanium slag is used as the raw material and, at the
same time, minimizes wastewater pollution. The waste
acid concentration obtained, which is at least 23% by
weight H_2SO_4 and preferably 24-27% by weight H_2SO_4 ,
10 enables the cost of treatment by recycling to be
distinctly reduced compared with the prior art.

The advantages of the process according to the
invention are illustrated by the following Examples.

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Example 1

1,170 kg titanium slag containing 75% by weight TiO_2
and 405 kg ilmenite containing 54% by weight TiO_2 were
20 digested with 1,996 kg 77.2% sulfuric acid and 970 kg 27%
oleum. (The 77.2% sulfuric acid had been recovered from
waste acid in accordance with US 4,502,976. It contained
5.8% by weight metal sulfates, including 345 ppm Cr in the
form of chromium sulfate and 36 ppm V in the form of
25 vanadium sulfate). The solid reaction product formed
during the digestion reaction was dissolved with 3.4 m³ of
the fraction C separated off during the washing of the
hydrolyzate of a preceding batch and 0.9 m³ wash solution
from the washing of the digestion residues. The solution
30 was filtered and the titanyl sulfate hydrolyzed.

Hydrolysis was carried out as follows:

49 l of a suspension of hydrolysis nuclei separately
produced by precipitation of titanyl sulfate with sodium
hydroxide were added to 4.35 m³ titanyl sulfate solution
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(corresponding to 1 t TiO_2). The mixture was brought to the boiling temperature by introduction of steam and boiled to the "match point". The introduction of steam was then interrupted for 30 minutes, after which more steam was introduced and the mixture boiled for 2.5 h. After a total process time of 2.5 h, 0.9 m³ solution which had been separated as fraction B during washing of the hydrolyzate was added. 70 minutes after addition of the solution, the introduction of steam was stopped. The hydrolysis yield was 95.4%.

The suspension obtained was filtered, waste acid containing 26.9% by weight H_2SO_4 accumulating as filtrate. The filter cake was then washed with water. The solution accumulating as filtrate during washing of the filter cake was divided into 4 fractions:

At the beginning of the washing process, the concentration of the solution fell slowly from 26.4 to 22-23% by weight H_2SO_4 and then rapidly to values below 5% by weight. The first 2.9 m³ filtrate were separated off as fraction A until a concentration of 23% by weight H_2SO_4 had been reached. This fraction had an average concentration of 24.6% by weight H_2SO_4 and was combined with the waste acid which had accumulated during filtration of the hydrolyzate suspension. The waste acid fed to the recycling process had an average concentration of 25.5% by weight H_2SO_4 , 345 ppm Cr and 580 ppm V. It contained 95.2% of the sulfate ions used during digestion of the raw material. 0.9 m³ of the filtrate were then separated off as fraction B while the concentration of the filtrate fell from 23 to 10.2% by weight H_2SO_4 . The fraction B had an average concentration of 19.6% by weight H_2SO_4 , 265 ppm Cr and 446 ppm V. It contained 9.3% of the sulfuric acid which was present in the suspension after hydrolysis. 2.4 m³ solution were then separated off as fraction C. This filtrate fraction had a concentration of 5.5% by weight H_2SO_4 , 19 ppm Cr and 32 ppm

V. It contained 5.4% of the sulfuric acid present on completion of hydrolysis.

When the filtrate stream was switched over as fraction D to the wastewater channel, the filtrate contained 3.1% by weight H_2SO_4 . The concentration fell to 0.3% by weight H_2SO_4 . 1.8% by weight of the sulfate ions used in the digestion of the raw material were removed.

The filter cake obtained after washing of the hydrolyzate was bleached by the addition of Al powder and sulfuric acid. The standardizing chemicals phosphoric acid, alkalis and rutile nuclei were then added to the filter cake, followed by calcination under standard conditions at $950^\circ C$ in a rotary kiln to form rutile pigment.

The pigment thus obtained was substantially identical with the typical standard of normal production where water rather than fraction B was added during hydrolysis and the digested material was dissolved with water.

Example 2

In the digestion of the raw material, the same ore mixture as in Example 1 was digested with 2,055 kg 77.2% recovered sulfuric acid and 1,000 kg oleum. The digestion cake was dissolved with 3.3 m^3 of the filtrate separated off as fraction C. The digestion yield was 0.3% higher than in Example 1.

Hydrolysis was carried out as in Example 1 with addition of 0.9 m^3 washing filtrate (fraction B). The hydrolysis yield was 95.7%. The suspension obtained was filtered. The waste acid accumulating had a concentration of 26.3% by weight H_2SO_4 . The filter cake was then washed with water and the washing filtrate separated into three fractions. Fraction A was separated off up to a concentration of 20.5% by weight H_2SO_4 . It had an average sulfuric acid content of 23.3% by weight and was combined with the waste acid which had previously accumulated. The waste acid

fed to the recycling process contained 24.7% by weight H_2SO_4 , 334 ppm Cr and 562 ppm V. It contained 97% of the sulfate ions used in digestion of the raw material; the remaining 3% were chemically fixed to the titanium oxide hydrolyzate.

After fraction A, 0.9 m³ filtrate were separated off as fraction B while the H_2SO_4 concentration fell from 20.5 to 6% by weight. Fraction B contained on average 17.8% by weight H_2SO_4 , corresponding to 9% of the total sulfuric acid present after hydrolysis.

3.3 m³ filtrate having an H_2SO_4 concentration between 6 and 0.4% by weight, average 1.7% by weight, were separated off as fraction C. It contained 2.5% of the sulfuric acid present on completion of hydrolysis.

The hydrolyzate was processed to rutile pigment as in Example 1. The pigment substantially corresponded to the production standard.

WHAT IS CLAIMED IS:

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1. A process for the production of titanium dioxide comprising digesting titanium raw materials with sulfuric acid, forming a titanyl sulfate solution by dissolution of the digested material, hydrolyzing the titanyl sulfate to form a suspension of hydrolyzate and metal-sulfate-containing sulfuric acid, the so-called waste acid, separating the hydrolyzate and waste acid, feeding the waste acid to a treatment or recycling process, washing the hydrolyzate and separating the washing liquid accumulating during the washing of the hydrolyzate into fractions of decreasing concentrations, and calcining the hydrolyzate to form TiO_2 pigment wherein the first fraction (A) of the separated fractions of the washing liquid is combined with waste acid and fed to the treatment or recycling process, the second fraction (B) is used instead of water in titanyl sulfate hydrolyses and the third fraction (C) is used to dissolve digested material from digestion of titanium raw material.

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2. A process according to claim 1, wherein a fourth fraction D separated from the washing of the hydrolyzate is used instead of water to wash hydrolyzate or is removed as wastewater.

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3. A process according to claim 1, wherein 80 to 93% of the sulfuric acid present in the suspension after hydrolysis of the titanyl sulfate is fed as waste acid

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5 to the treatment or recycling process, 4 to 12% of the
sulfuric acid is returned to hydrolysis of the titanyl
sulfate and 1 to 5% of the sulfuric acid is used to
dissolve the digested material.

10 4. A process according to claim 1, wherein 0.1
to 5% of the sulfuric acid is used to wash the hydro-
lyzate or is removed as waste water.

15 5. A process according to claim 1, wherein the
waste acid fed to the treatment or recycling process has
a concentration of at least 23% by weight H_2SO_4 .

20 6. A process according to claim 5, wherein the
waste acid fed to the treatment or recycling process has
a concentration of at least 24% by weight H_2SO_4 .

25 7. A process according to claim 1, wherein the
fraction B from washing of the hydrolyzate returned to
the hydrolysis of titanyl sulfate contains 7 to 23% by
weight H_2SO_4 .

8. A process according to claim 1, wherein the
fraction C used to dissolve the digested material con-
tains 0.2 to 7% by weight H_2SO_4 .

30 9. A process according to claim 1, comprising
carrying out the hydrolysis of titanyl sulfate using
separately produced hydrolysis nuclei and adding
fraction B after at least 50% of the total duration of
the hydrolysis process has elapsed.

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